

original article

A mathematical model for predicting 24-h variations of BTEX concentrations in ambient air of Tehran

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ABSTRACT

Aims: In this study, the temporal variations of Benzene, Toluene, Ethyl benzene and Xylene (BTEX) in the atmosphere of Tehran city was investigated.

Materials and Methods: Two air quality monitoring stations, Aghdasieh and Ray, in different locations of the city were selected. Sampling was carried out hourly from Nov 23, 2007 to Dec 22, 2007 in Aghdasieh air monitoring station and from Dec 10, 2007 to Jan 9, 2008, in Ray's air monitoring station by an online BTEX monitoring system. The correlations, repeated measures variance and regressions tests were used for statistical analysis.

Results: Results indicated that, concentrations of these compounds were sometimes higher than standard limits and were significantly different in selected stations. However, an approximately similar increasing and decreasing trend was seen among them. In most cases, equations for concentration variations were sinusoidal or fourth-order.

Conclusion: According to the results, sinusoidal and fourth-order are most suitable equations for BTEX concentration variations in the ambient air of the city, and the trends of variations are similar in different places of the city.

Key words: Air pollution, air quality modeling, ambient air, BTEX, concentration variations, tehran, VOCs

INTRODUCTION

Air pollution is one of the main problems related to increased rate of industrialization and considerable use of motor vehicles. Tehran, a sizeable city with around 10 million population, is located in the north of the central plateau of Iran (35° 45' North 51° 30' East). Sometimes, air pollution

is high in this city and the city is often covered with smog. Tehran is bounded in the north by the Alborz Mountain, which prevents the flow of the humid Caspian air from entering into the central plateau of Iran. This is a cause of thermal inversion, frequently observed, that traps Tehran's air.^[1] This less humidity and infrequent clouds, therefore, make Tehran quite a sunny city. Besides, ultraviolet radiations combined with existing pollutants, especially hydrocarbons and NO_x, significantly raises the ozone level.^[2]

Highly populated metropolitan areas, called megacities, usually encounter to high levels of air pollutants.^[3] Tehran, as the capital of Iran, is also involved with this problem.^[4] Main air pollution sources in Tehran are industrial venues and motor vehicles.^[5,6] Studies showed the relationship of

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traffic and location with volatile organic compounds (VOCs) concentrations.^[7] These sources release several pollutants into the atmosphere. One of these harmful pollutants is BTEX. It includes benzene, toluene, ethyl benzene and xylene. These chemicals have been detected together in environmental studies and all of them are VOCs.^[8] These compounds are released into the ambient air due to combustion of petroleum derivatives and industries.^[9] They are harmful for human health even in low levels.^[10,11] Benzene is a carcinogenic compound and toluene is suspected to be carcinogenic.^[12] The main source of BTEX in the urban air is combustion emissions from automobile exhaust pipes.^[13] Different international organizations such as the centers for disease control and prevention (CDC), environmental protection agency (EPA), and world health organization (WHO) have set guidelines and standards for these pollutants because of their significant health effects. Surveying, modeling, and controlling the concentration of these compounds are, therefore, important to decrease their health effects. Some studies have tried to model the air pollutants' concentration, such as NO₂, CO₂ and so on, according to meteorological conditions and geographical situations.^[14-17] However, the BTEX concentrations' trend of variation has not been studied itself. In this study, 24-h variations of BTEX concentrations in ambient air of Tehran were surveyed to determine the rhythm and the levels of these variations.

MATERIALS AND METHODS

In this cross-sectional study, two air quality monitoring stations in two different locations in the city were used, with around 21 km distance from each other and not precisely synchronic, to have a different situation in two stations. Figure 1 shows the locations of the sampling stations. The data were obtained from 24-h sampling carried out on a monthly basis for Aghdasieh (Nov 23, 2007 to Dec 22, 2007) and Ray (Dec 10, 2007 to Jan 9, 2008). The concentration values were measured by an online monitoring system, VOC71M-PIB BTEX Analyzer (France), by which BTEX concentrations in ambient air are automatically measured. The number of surveyed samples were 5328 per month. The correlations, repeated measures variance and regressions test were used in order to statistical analyses applied to the data were correlations, repeated measures variance and regressions. These analyses were performed by use of SPSS, Excel and curve expert.

RESULTS

The mean hourly concentration of BTEX at Aghdasieh and Ray stations are given in Figure 2. Results indicated that the concentrations of these compounds experience similar trends in both stations. From midnight to 8.00 in local time, there was a decreasing trend in concentrations. Then, the concentrations rose until 11.00, dropped until 18.00, and again rose until 23.00. However, the concentrations of

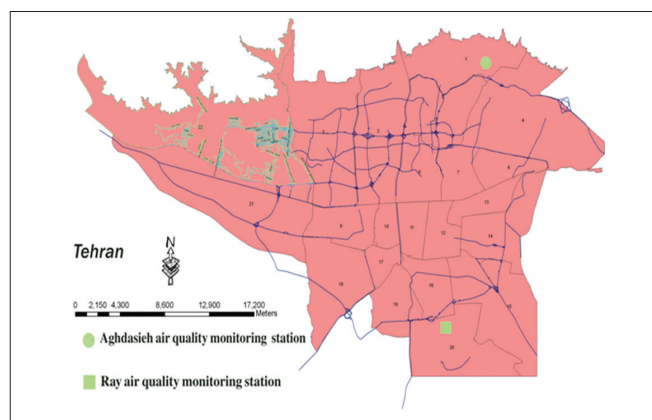


Figure 1: The location of Aghdasieh and Ray air quality monitoring stations in Tehran city

toluene at Aghdasieh station did not follow this trend and its maximum and minimum concentrations were different from other pollutants in both stations. The other important point is that the temporal peak values for benzene and xylene at Aghdasieh station occurred at midnight, but the temporal peak concentrations for toluene and ethyl benzene at Aghdasieh station and all four compounds at Ray station occurred at 9.00.

According to correlation analysis, there were significant relationships between each day's hourly concentrations of the BTEX compounds and mean value of each pollutant's hourly concentration for duration of study ($P < 0.05$). In most cases, the significance value was higher than the level of significance ($P < 0.01$), and significantly reverse correlation was seen only in 2 days at Aghdasieh air monitoring station. The repeated measures analysis of variance conducted for BTEX concentrations during the day in a month showed that there was significant difference among hourly concentration during the day. The results are given in Table 1. According to Table 1, the results do not show any significant difference between toluene concentrations at different times at Aghdasieh air monitoring station. It can be seen from the results of this analysis that some equations significantly fit with the variations of BTEX concentrations during the days ($P < 0.05$). The related equations for BTEX in each air monitoring station are given in Table 2. Furthermore, the regression analysis showed that the hourly variations of pollutant concentrations have significant relationship with sinusoidal curves. Figure 3 is an example of the curves obtained from this analysis. The value of coefficients and constants for the obtained equations are given in Table 3.

The correlation among mean concentrations of pollutants in each station and between two stations showed significant relationships ($P < 0.01$). However, toluene concentration had reverse correlation in the Aghdasieh station compared to xylene in the Ray station and had not have any positive correlation with other pollutants in this study. Results of data analysis showed that the concentrations of pollutants are significantly different between the two stations except

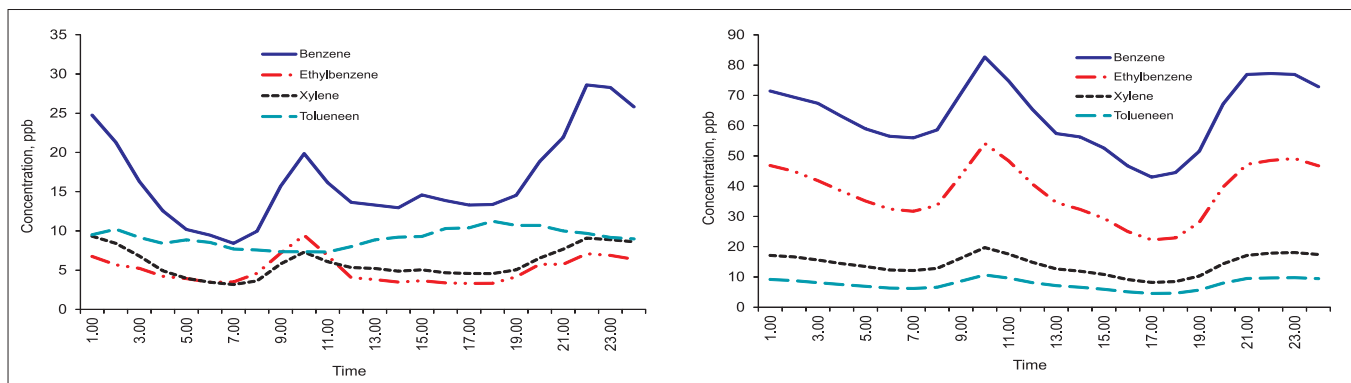


Figure 2: Average temporal variations of BTEX concentrations at: (a) Aghdasieh, (b) Ray

Table 1: Significant difference between concentrations of BTEX in the different hours of day																								
Time	00:00	1:00 AM	2:00 AM	3:00 AM	4:00 AM	5:00 AM	6:00 AM	7:00 AM	8:00 AM	9:00 AM	10:00 AM	11:00 AM	12:00 AM	1:00 PM	2:00 PM	3:00 PM	4:00 PM	5:00 PM	6:00 PM	7:00 PM	8:00 PM	9:00 PM	10:00 PM	11:00 PM
00:00	-	B	BX	BX	BEX	BtEeX	X							E	ex	tex	EX	EX	X					
1:00 AM		-	B	BX	BX	BtX	BteX	X									ex	X						
2:00 AM			-	EX	BX	BEX	BX	X																
3:00 AM				-																				
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5:00 AM						-																		
6:00 AM							-		B	Btex	Bte	B				B	B	B	B	B	Bt	BX	X	BX
7:00 AM								-	t	BbttexX	betXx	X									BX	BtX	X	BX
8:00 AM									-	teXx	X											X	X	X
9:00 AM												-												
10:00 AM													-			btex	btex	Tex						
11:00 AM														-		btex	btex	Btex						
12:00 AM															-	tex	tex	Tex				x		E
1:00 PM																	ex	Tex				x	X	E
2:00 PM																	x	Tex				tex		E
3:00 PM																-	btex				x	btex	btEeXx	tEeXx
4:00 PM																	-			btex	btex	btEex	btEex	tEex
5:00 PM																		-		btex	tex	btEeXx	btex	tEeXx
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7:00 PM																					-	teXx	e	
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10:00 PM																							-	
11:00 PM																								-

Each letter is representative of concentration of one pollutant in one monitoring station. Appearance of each letter in the cells of crisscross table shows that, concentrations of pollutants were significantly different between related times. B = Benzene in Aghdasieh, T = Toluene in Aghdasieh, E = Ethyl benzene in Aghdasieh, X = Xylene in Aghdasieh, b = Benzene in Ray, t = Toluene in Ray, e = Ethyl benzene in Ray, x = Xylene in Ray

Table 2: Equations for hourly variation of BTEX concentrations						
Station	Pollutant	P-value				
		Linear	Second order	Third order	Fourth order	Higher orders
Aghdasieh	Benzene	0.025	<0.01	-	<0.01	<0.01
	Toluene		-	<0.01	-	-
	Ethyl benzene		<0.01	-	<0.01	<0.01
	Xylene		<0.01	-	<0.01	<0.01
Ray	Benzene		<0.01	0.03	0.043	<0.01
	Toluene		<0.01	0.031	<0.01	<0.01
	Ethyl benzene		<0.01	0.03	<0.01	<0.01
	Xylene		<0.01	0.014	<0.01	<0.01

for toluene. The mean concentrations of BTEX in the two studied air quality monitoring stations are given in Table 4. The mean concentrations of benzene, ethyl benzene, and

xylene at Ray station were higher than those at Aghdasieh station, while the mean concentration of toluene at Aghdasieh was higher than that at Ray.

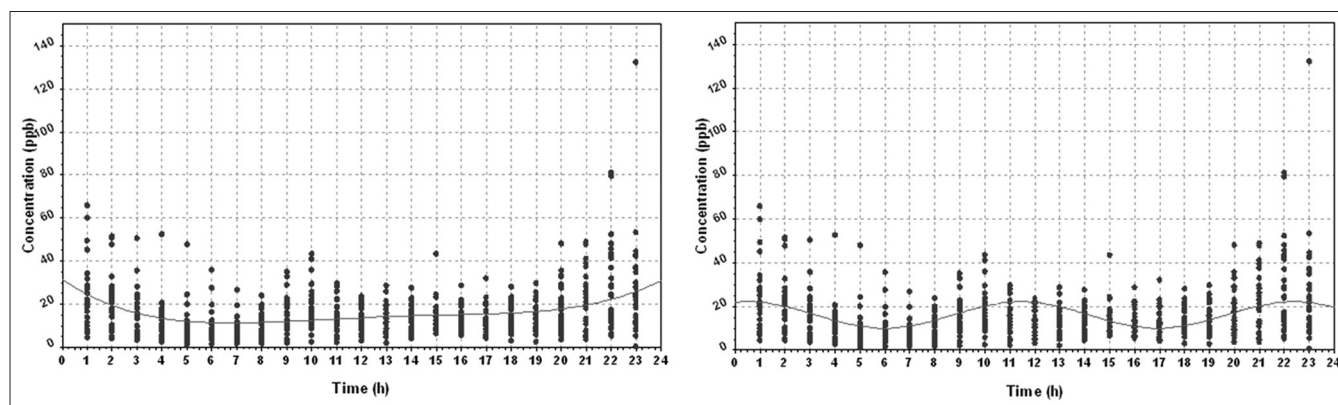


Figure 3: Regression lines for hourly variations of benzene concentrations at Aghdasieh air quality monitoring station, (a) fourth order curve, (b) sinusoidal curve

Table 3: Constants and coefficients of obtained equations for hourly variation of BTEX concentrations

Station	Pollutant	Equation	Constants and coefficients
Aghdasieh	Benzene	Sinusoidal	$a = 16.15, b = 6.016, c = 0.57, d = -0.28$
		Fourth Order	$a = 31.51, b = 10.71, c = 0.57, d = -0.058, e = 0.00114$
	Ethyl benzene	Sinusoidal	$a = 5.013, b = 1.87, c = 0.56, d = 0.307$
		Fourth Order	$a = 7.06, b = -1.13, c = 0.195, d = -0.013, e = 0.000293$
	Xylene	Sinusoidal	$a = 5.77, b = 2.12, c = 0.587, d = -0.528$
Ray	Toluene	Fourth Order	$a = 12.3, b = -3.09, c = 0.416, d = -0.0225, e = 0.000434$
		Sinusoidal	$a = 9, b = 1.62, c = 0.317, d = 0.357$
	Benzene	Third Order	$a = 11.9, b = -1.35, c = 0.127, d = -0.00317$
		Sinusoidal	$a = 62.44, b = 12.89, c = 0.57, d = -0.0253$
	Ethyl benzene	Fourth Order	$a = 68.71, b = -2.28, c = 0.5, d = -0.045, e = 0.00123$
		Sinusoidal	$a = 37.57, b = -7.91, c = 1.07, d = -0.149$
	Xylene	Fourth Order	$a = 50.66, b = -5.79, c = 0.99, d = -0.07, e = 0.00163$
		Sinusoidal	$a = 13.9, b = 3.75, c = 0.569, d = -0.126$
	Toluene	Fourth Order	$a = 18.22, b = -1.77, c = 0.313, d = -0.023, e = 0.000557$
		Sinusoidal	$a = 7.48, b = 2.14, c = 0.57, d = -0.108$
		Fourth Order	$a = 10.03, b = -1.24, c = 0.215, d = -0.015, e = 0.000342$

Table 4: BTEX concentrations in Aghdasieh and Ray air quality monitoring stations

Station	Pollutant	Mean (ppb)	Std. deviation
Aghdasieh	Benzene	16.5708	5.85699
	Ethyl benzene	5.0763	1.67230
	Xylene	5.9563	1.89337
	Toluene	9.1058	1.16379
Ray	Benzene	63.2408	11.18554
	Ethyl benzene	38.2271	9.08493
	Xylene	14.1271	3.28732
	Toluene	7.6038	1.77596

DISCUSSION

According to the significant correlation between variations in concentrations of each pollutant on an hourly basis and its mean for each pollutant during the period of sampling (a month), it can be implied that the mean values diagram of BTEX can represent hourly variations in surveying the trend of variations in concentration in this study. Therefore, we can estimate the hourly variation curve of concentrations for these pollutants according to the results of regression analysis, which are represented in Table 2. The following conclusions are presented according to this estimation.

Because of the significant differences among concentrations of benzene at Aghdasieh air monitoring station, the trend of the variation does not obey the linear regression and second order equation. Hence, it can be concluded that the concentrations obey the fourth- and higher- order equations. Since there is a significant difference between the concentrations reported for 21.00, 22.00, and 23.00 clock hours, when the drop in concentrations occurred, this drop could tend the equation of the curve to fifth or higher orders. According to the principle of parsimony, however, the higher-order equations are not used in the results of this study (Ajai and Sanjaya, 2006). Therefore, a fourth-order equation ($y = a + bx + cx^2 + dx^3 + ex^4, r = 0.4, t = 11.09$) and sinusoidal equation ($r = 0.34, t = 9.18, y = a + b \cdot \cos(cx + d)$) are more reliable. The t -value is observed value of the t -statistic that is used to test the hypothesis that two attributes are correlated. A t -value far from 0, either positive or negative, is evidence for that there is a correlation between the attributes. The t -value was calculated by equation (1):^[18]

(1) ;Where “ r ” is the correlation coefficient and “ n ” is the number of input value pairs.

As described above, for benzene at Ray station, like that at

Aghdasieh station, the fourth-order equation ($r = 0.165$, $t = 4.33$) and the sinusoidal equation ($t = 6.06$, $r = 0.228$) were obtained. In these equations, “ r ” in sinusoidal equation is higher than that in fourth-order equation. However, due to absence of significant differences among concentrations in the first hours, the fourth-order equation that is softer in the first section is more reliable. For ethyl benzene at Aghdasieh air monitoring station, a sinusoidal relationship ($r = 0.29$, $t = 8.11$) and a fourth-order equation ($r = 0.18$, $t = 4.9$) were obtained. For ethyl benzene at Ray air monitoring station, a sinusoidal equation ($t = 7.14$, $r = 0.26$) and a fourth-order equation ($r = 0.199$, $t = 5.25$) were obtained. For xylene at Aghdasieh air monitoring station, a fourth-order equation ($r = 0.415$, $t = 10.93$) and a sinusoidal equation ($r = 0.405$, $t = 10.61$), while at Ray air monitoring station, a fourth-order equation ($r = 0.249$, $t = 6.77$) and a sinusoidal equation ($r = 0.202$, $t = 5.43$) were obtained. As stated above, there were no significant differences among concentrations in the first hours of days. Therefore, a fourth-order equation is more suitable to forecast hourly variations of xylene at Ray station. For toluene at Aghdasieh air monitoring station, a third-order equation ($t = 3.85$, $r = 0.15$, $y = a + bx + cx^2 + dx^3$) and a sinusoidal equation ($r = 0.162$, $t = 4.17$) were obtained. At Ray air monitoring station, a fourth-order equation ($r = 0.189$, $t = 5.07$) and a sinusoidal equation ($r = 0.26$, $t = 7.09$) were obtained for Toluene.

The results showed that the variation of BTEX concentrations in most cases obey the sinusoidal and fourth-order equations. Although the significant differences among the concentration of pollutants on different days had affected the coefficients of these equations, especially “ a ” that is the intercept of equation, application of these equations to forecast the pollutants hourly concentrations, can be useful for determining critical times during the day. This prediction can be applied in air pollution control and management of social activities, especially when high concentrations are forecasted. Results of a study carried out by Martinez^[19] showed that the variation trend of VOCs concentration is at its peak at 9.00 o'clock in the morning, which is similar to those for Ray air monitoring station. A correlation between mean values of hourly BTEX concentration in a suburban area and its neighborhoods is also obtained.^[3] The correlation obtained is similar to our findings.

The two selected air monitoring stations in the present study are quite far apart. Aghdasieh air monitoring station is located in the north and Ray air monitoring station is located in the southern end of the city. They also have different altitudes and local conditions, different industrial venues and different levels of urban traffic that can affect concentrations of the pollutants.^[6] The results of this study indicated a significant difference among concentrations of the pollutants between the two air monitoring stations. According to the results of this study, however, variation trend of BTEX concentrations is similar at both air monitoring stations.

CONCLUSIONS

The two selected air monitoring stations in the present study are quite far apart. Aghdasieh air monitoring station is located in the north and Ray air monitoring station is located in the southern end of Tehran. They also have different altitudes, local conditions, and different levels of urban traffic that can affect concentrations of the pollutants. Despite these, according to the results of this study, it can be concluded that the variations trend of BTEX concentrations, during the day, in different locations, are almost similar and often obey the fourth-order and sinusoidal equations. Moreover, determination of effective coefficients such as intercept “ a ” is an important factor for prediction of the BTEX concentrations during the day.

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